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ELASTIC BEHAVIOUR OF MATTER UNDER VERY HIGH PRESSURES

Uniform Compression

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1. Introduction

The elastic behaviour of substances, which are already in a highly strained state, is a subject of considerable importance, in its fundamental aspects as well as in its application to important questions like the constitution and stability of massive entities such as exist in the interior of the Earth. In a paper entitled 'Elasticity and Constitution of the Earth's Interior,' Birch (1952) has given a comprehensive account of this problem. Matter in the interior of the Earth is subjected to large stresses, resulting in an accumulation of great amounts of strain energy. It is known that periodical releases of the strain energy, thus accumulated, manifest themselves as earthquakes in various regions, although the exact causes thereof and the detailed mechanism of these energy releases, are still matters open for further study. It is also known that shear waves are not sustainable in the interior of the Earth below a depth of about 3,000 km., while up to that depth from the surface, compressional as well as shear waves are present. An explanation of these remarkable phenomena would necessarily involve a knowledge of the elastic behaviour of matter at the depths in question. Thus, the first step in this direction would be the evaluation of the elastic constants of substances, which are already under great strains, in terms of known parameters.

When considering such large strains, one has to have recourse to the finite or non-linear theory of elasticity, an exact development of which in matrix form has been given by Murnaghan (1951). When the strain components are large, the stress at a point is no longer a linear function of the strain components at that point, but includes quadratic terms as well, and the strain energy function ϕ has to be extended to include at least the cubic powers of the strain components. The coefficients of the quadratic terms have been called 'the Second Order Elastic Constants' and of the cubic terms, 'the Third Order Elastic Constants'. Birch (1947, 1952), Fumi

(1951), Hearmon (1953) and Bhagavantam (1949, 1957) have dealt with this problem and have derived the independent third order constants for the various crystal classes. In the present work, a reference to these investigations will become necessary as the strain energy includes second as well as third order elastic constants.

In studying the elastic response of a substance which is initially subjected to a finite strain, additional strains can always be visualized as infinitesimal in character, since the case of a finite strain superposed over another finite strain can be reanalyzed so as to correspond to an infinitesimal strain imposed on a finite one. As this additional strain is infinitesimal, its effect in the strain energy function will be limited to quadratic terms only, the coeffiicients of which will be the elastic constants appropriate to the substance in the prestressed state. We shall designate these as the 'effective elastic constants'. They completely specify the elastic response of a substance in a state of finite strain, when additional infinitesimal strains are superposed thereon. These effective constants will depend on the second and third order elastic constants of a stress-free state and also upon the state of initial stress.

Expressions for such effective elastic constants can be derived by noting that the elastic energy of the infinitesimal deformation must be equal, after multiplication by a suitable magnification factor and allowing for the work done by the external forces, to the difference in the total energy of the system when subjected, firstly to the finite strain, and secondly to the finite *plus* infinitesimal strain considered as a single composite state of strain. The magnification factor arises because the strain energy always refers to a unit initial volume and this volume is different according as whether we choose our initial state as the stress-free state or as a state of finite initial stress. It will be observed from the details given in the following that this method of evaluating the elastic constants from the use of the energy difference, adopted in the present paper, is much simpler than the method of evaluating them from the Stress Matrix—a procedure adopted by some earlier workers (Birch, 1947; Hughes and Kelly, 1953). There is a discrepancy between the values obtained by us in this paper and by Birch (1947) and a discussion of the same is also given.

It has to be mentioned here that Green and Zerna (1954) have considered the question of superposition of an infinitesimal deformation over a triaxial finite strain for an isotropic substance but their treatment does not explicitly bring in the third order elastic constants. We have explicitly considered these constants and studied in detail the case of cubic symmetry

because such a case would pertain closely to substances which actually occur in nature. In the present paper we have also included, in a tentative and general way, the indications which the energy function would give regarding the anomalous behaviour of matter subjected to high pressures. Detailed discussions of this aspect involve the Theory of Dynamical Elasticity, a topic which we propose dealing with in a subsequent paper.

2. Finite Deformation Theory

We now proceed to give the formalism of the finite deformation theory to the extent required for our problem. By a deformation, we mean that the internal constituent points in a body have undergone displacements with respect to each other, so that their relative distances have altered. To specify such an alteration in the distance between a point P and every other point Q, R, S, etc., in its neighbourhood, we first note that the general expression for an infinitesimal length appears as a quadratic ($ds^2 = dx^2 + dy^2 + dz^2$). If therefore ds_0 is the length PQ before deformation and ds the same length after deformation, half the alteration in the square of the length, $(ds^2 - ds_0^2)/2$ is taken as a measure of the state of strain of the distance PQ in question. By assigning general positional co-ordinates to Q, the alteration in length not only of PQ but of every other length PR, PS, etc., in the neighbourhood of P is obtained, so that the state of strain around P is completely specified by the quadratic form $(ds^2 - ds_0^2)/2$. To derive an expression for this quantity, we note that, if as a result of the deformation, a point with initial co-ordinates (a, b, c) referred to any convenient space fixed Cartesian co-ordinate system moves over to a final position (x, y, z) referred, for convenience to the original frame, we can introduce a displacement vector with components (u, v, w) given by $x = a + u$, $y = b + v$, $z = c + w$, where u, v, w are functions of the initial positional co-ordinates (a, b, c). If the point P, with co-ordinates (a, b, c) moves over, as a result of deformation to P′ with co-ordinates $(x, y, z) = (a + u, b + v, c + w)$, the point Q in the infinitesimal neighbourhood of P with co-ordinates say $(a + da, b + db, c + dc)$ will move over to the position $(x + dx, y + dy, z + dz)$ where dx, dy, dz are given by the relations

$$
\begin{aligned}
dx &= \left(1 + \frac{\partial u}{\partial a}\right) da + \frac{\partial u}{\partial b} \cdot db + \frac{\partial u}{\partial c} \cdot dc \\
dy &= \frac{\partial v}{\partial a} \cdot da + \left(1 + \frac{\partial v}{\partial b}\right) db + \frac{\partial v}{\partial c} \cdot dc \\
dz &= \frac{\partial w}{\partial a} \cdot da + \frac{\partial w}{\partial b} \cdot db + \left(1 + \frac{\partial w}{\partial c}\right) dc.
\end{aligned} \tag{1}
$$

The nine derivatives $\partial u/\partial a$, etc., completely specify the most general displacements, including rotations of the element as a whole, in which the relative distances of points within the element are not altered. There is therefore no room for play of the elastic forces within the element, and one could then remove the effect of rotations by the removal of the antisymmetric part in the equations by employing the usual methods. This will leave only 6 independent combinations of the displacement derivatives to be considered in the elastic deformation. If we take it that the rotations are zero, this will immediately require that $\partial u/\partial b = \partial v/\partial a$, etc., so that the matrix of the transformation is symmetric as it stands with six independent components. In the linear or infinitesimal theory of elasticity, the strain components are identified with these six independent displacement derivatives $\partial u/\partial a$, $\partial v/\partial b$, etc. In the finite or non-linear theory of elasticity, however, we work out $(ds^2 - ds_0^2)/2$ using relation (1) and noting that $ds^2 = dx^2 + dy^2 + dz^2 =$ square of length PQ after deformation and $ds_0^2 = da^2 + db^2 + dc^2 =$ square of length PQ before deformation. This quadratic form therefore appears as

$$\frac{ds^2 - ds_0^2}{2} = \eta_{11}da^2 + \eta_{22}db^2 + \eta_{33}dc^2 + 2\eta_{12}dadb + 2\eta_{23}dbdc + 2\eta_{31}dcda \tag{2}$$

where

$$\eta_{11} = \frac{\partial u}{\partial a} + \frac{1}{2}\left[\left(\frac{\partial u}{\partial a}\right)^2 + \left(\frac{\partial v}{\partial a}\right)^2 + \left(\frac{\partial w}{\partial a}\right)^2\right] \tag{3}$$

with similar equations for η_{22} and η_{33}, and

$$\eta_{12} = \eta_{21} = \frac{1}{2}\left(\frac{\partial v}{\partial a} + \frac{\partial u}{\partial b}\right) + \frac{1}{2}\left(\frac{\partial u}{\partial a}\cdot\frac{\partial u}{\partial b} + \frac{\partial v}{\partial a}\cdot\frac{\partial v}{\partial b} + \frac{\partial w}{\partial a}\cdot\frac{\partial w}{\partial b}\right) \tag{4}$$

with similar equations for η_{23}, η_{31}, etc.

The η's are thus coefficients in a certain quadratic form expressing the change in the squared length and they constitute the 9 entities of a (3, 3) matrix styled as the strain matrix. In view of the symmetry of this matrix, the 9 components reduce to 6 and a convenient representation of the strain matrix is

$$\eta = \begin{pmatrix} \eta_1 & \eta_6 & \eta_5 \\ \eta_6 & \eta_2 & \eta_4 \\ \eta_5 & \eta_4 & \eta_3 \end{pmatrix}. \tag{5}$$

It is evident from (3) and (4) that when the squares and products of the displacement derivatives $\partial u/\partial a$, etc., are neglected, the strain matrix of the finite theory becomes identical with the infinitesimal matrix. In view of the respective definitions, one can also say that in the infinitesimal theory, it is of no consequence whether the displacement derivatives are calculated at the initial or final positions of a point and the initial and final positions are thus interchangeable. In the finite theory, however, the distinction between the initial and final states has to be maintained.

The displacement of a point from an initial position (a, b, c) to the final position (x, y, z), as given in equation (1), is most conveniently represented by the transformation $x = \mathrm{J}a$, $(x = x, y, z)$, $(a = a, b, c)$ and J, the Jacobian of the transformation is given from (1) by

$$\mathrm{J} = \begin{pmatrix} 1+\dfrac{\partial u}{\partial a} & \dfrac{\partial u}{\partial b} & \dfrac{\partial u}{\partial c} \\ \dfrac{\partial v}{\partial a} & 1+\dfrac{\partial v}{\partial b} & \dfrac{\partial v}{\partial c} \\ \dfrac{\partial w}{\partial a} & \dfrac{\partial w}{\partial b} & 1+\dfrac{\partial w}{\partial c} \end{pmatrix} = \begin{pmatrix} \dfrac{\partial x}{\partial a} & \dfrac{\partial x}{\partial b} & \dfrac{\partial x}{\partial c} \\ \dfrac{\partial y}{\partial a} & \dfrac{\partial y}{\partial b} & \dfrac{\partial y}{\partial c} \\ \dfrac{\partial z}{\partial a} & \dfrac{\partial z}{\partial b} & \dfrac{\partial z}{\partial c} \end{pmatrix}. \qquad (6)$$

Denoting by J^* the transpose of this matrix, it is evident that if we form the product matrix $\mathrm{J}^*\mathrm{J}$, subtract unity from each of the 3-diagonal elements and halve the result, we get the matrix of coefficients of the quadratic form (2) and this is the strain matrix (5). Murnaghan (1951) has employed this form as the definition of the strain matrix in the following way.

$$\eta = \tfrac{1}{2}(\mathrm{J}^*\mathrm{J} - \mathrm{E}_3). \qquad (7)$$

In (7), E_3 is the unit matrix of dimension 3. We also note here that the subtraction of E_3 indicates that the original length is being subtracted from the new or altered length between two points, which means that in our treatment, we are excluding all such displacements which keep the relative distance between every two points within an element unaltered. Rotations are displacements of this type, and in the finite theory, the removal is effected from the product matrix $\mathrm{J}^*\mathrm{J}$ and not from J itself as in the infinitesimal theory. J thus need not be a symmetric matrix, nor is it rendered so, in the finite theory. A simple shear given by

$$x = a + \eta b,\ y = b,\ z = c,$$

is an example of an unsymmetrical J. However the strain matrix formed from the same by the formula $\eta = \tfrac{1}{2}(\mathrm{J}^*\mathrm{J} - \mathrm{E}_3)$ is symmetric. When

formulating the most general displacement, we must therefore take J with 9 independent components (and not reduce to 6 by removal of the anti-symmetric part), so long as finite deformations are concerned. We shall have occasion to refer to this question again at a subsequent stage in this paper.

3. STRAIN ENERGY EXPRESSION IN THE FINITE THEORY, WITH AND WITHOUT AN INITIAL STRESS

The strain energy ϕ, measured per unit volume of the initial state, would be a function of the 6 strain components $\eta_1 \ldots \eta_6$, and can therefore be expanded as a power series in the η's.

$$\phi = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \ldots\ldots \tag{8}$$

The constant ϕ_0 has no significance for us, as we are interested only in the derivatives of ϕ. The first order term ϕ_1 will be a linear function of the η's of the form

$$\phi_1 = c_1\eta_1 + c_2\eta_2 + c_3\eta_3 + 2c_4\eta_4 + 2c_5\eta_5 + 2c_6\eta_6. \tag{9}$$

In the infinitesimal theory of elasticity, the 6 components of stress $T_1, T_2, \ldots T_6$ corresponding to the 6 independent elements in the (3, 3) symmetric stress matrix T_{ik} are obtained as the derivatives of ϕ with respect to the corresponding strain component

$$T_{ik} = \frac{\partial\phi}{\partial\eta_{ik}}. \tag{10}$$

Like the strain tensor, we use here the notation $T_{11} = T_1$, $T_{22} = T_2$, $T_{33} = T_3$, $T_{23} = T_{32} = T_4$, $T_{31} = T_{13} = T_5$, $T_{12} = T_{21} = T_6$. In the finite theory, the stresses are given, as shown by Murnaghan, as the elements in the matrix derived from the formula

$$\mathbf{T} = \frac{\rho_x}{\rho_a}\,\mathbf{J}\,\frac{\partial\phi}{\partial\eta}\,\mathbf{J}^*. \tag{11}$$

Here ρ_x is the density of a volume element after deformation while ρ_a is its density before the deformation. If V_x and V_a be the corresponding volumes per unit mass of the substance, we have the relations

$$\frac{\rho_x}{\rho_a} = \frac{V_a}{V_x} = \frac{1}{\text{Determinant J}}. \tag{12}$$

To apply formula (11), we have to first write out the energy as a function of all the 9 strain components η_{ik}, *i.e.*, disregarding the symmetry relation $\eta_{ik} = \eta_{ki}$. Same procedure has to be adopted when applying (10) and (9) as well. From this the energy derivative matrix $\partial\phi/\partial\eta_{ik}$ has to be obtained and the product matrix of J, $\partial\phi/\partial\eta$ and J* be formed. This has to be finally multiplied by $\rho_x/\rho_a = (1/\text{det. J})$. Such calculations are in general laborious.

Whether the stress formula is regarded as based on (10) or (11), it is easy to see, on differentiating ϕ, that the first order coefficients $c_1, c_2 \cdots c_6$ must be equal to the initial stress components $T_1^0, T_2^0 \cdots T_6^0$ whenever such stresses are present. When we consider the superposition of strains $\delta\eta_1, \delta\eta_2 \cdots \delta\eta_6$ over finite strains $\eta_1^0, \eta_2^0 \cdots \eta_6^0$ caused by stresses $T_1^0, T_2^0 \cdots T_6^0$, the general form of ϕ_1 will be

$$\phi_1 = T_1^0\delta\eta_1 + T_2^0\delta\eta_2 + T_3^0\delta\eta_3 + 2T_4^0\delta\eta_4 + 2T_5^0\delta\eta_5 + 2T_6^0\delta\eta_6. \tag{13}$$

When the initial stress is a uniform hydrostatic pressure P, which is the case under consideration in the present paper,

$$\phi_1 = -P(\delta\eta_1 + \delta\eta_2 + \delta\eta_3) \tag{14}$$

$-P$ being used for the stress, since P is generally kept positive. This first order term in the energy will not occur whenever the energy is measured from an initial state of zero stress.

The second order energy ϕ_2, being a quadratic form in the η's, contains as coefficients the usual second order elastic constants, which correspond with the generalized Hooke's Law, while the third order term ϕ_3 contains the third order elastic constants as already mentioned, these coming into play when the strains are large. Following Birch (1947) and Hearmon (1953), we can write the full energy expression for a substance of cubic symmetry, when the strains are all measured from the state of zero strain, *i.e.*, a stress-free state, as

$$\begin{aligned}\phi &= \phi_2 + \phi_3 \\ &= \frac{c_{11}}{2}(\eta_1^2 + \eta_2^2 + \eta_3^2) + c_{12}(\eta_1\eta_2 + \eta_2\eta_3 + \eta_3\eta_1) \\ &\quad + 2c_{44}(\eta_4^2 + \eta_5^2 + \eta_6^2) + C_{111}(\eta_1^3 + \eta_2^3 + \eta_3^3) \\ &\quad + C_{112}\{\eta_1\eta_2(\eta_1 + \eta_2) + \eta_2\eta_3(\eta_2 + \eta_3) + \eta_3\eta_1(\eta_3 + \eta_1)\} \\ &\quad + C_{123}\eta_1\eta_2\eta_3 + C_{456}\eta_4\eta_5\eta_6 + C_{144}(\eta_1\eta_4^2 + \eta_2\eta_5^2 + \eta_3\eta_6^2) \\ &\quad + C_{155}\{\eta_1(\eta_5^2 + \eta_6^2) + \eta_2(\eta_4^2 + \eta_6^2) + \eta_3(\eta_4^2 + \eta_5^2)\}. \quad (15\end{aligned}$$

This contains 3 second order constants and 6 third order constants. The general method followed in writing the third power terms is to expand ϕ_3 and write it as $\Sigma C_{pqr}\eta_p\eta_q\eta_r$, where p, q, r take any values 1 to 6 subject to the condition $p \leq q \leq r$.

When we consider the case of superposition of an infinitesimal deformation $\delta\eta$ over an initial state of finite strain η corresponding to an initial hydrostatic pressure P, the energy for the $\delta\eta$ deformation should be written, to be consistent with the above formulation, as

$$\phi' = \phi'(\delta\eta) = -\mathrm{P}(\delta\eta_1 + \delta\eta_2 + \delta\eta_3) + \frac{b_{11}}{2}(\delta\eta_1^2 + \delta\eta_2^2 + \delta\eta_3^2) +$$

$$b_{12}(\delta\eta_1\delta\eta_2 + \delta\eta_2\delta\eta_3 + \delta\eta_3\delta\eta_1) + 2b_{44}(\delta\eta_4^2 + \delta\eta_5^2 + \delta\eta_6^2). \quad (16)$$

The higher powers are neglected as the deformation $\delta\eta$ is treated as infinitesimal. The $\delta\eta$ are measured from the η state and the energy is per unit volume of this η state.

4. Evaluation of the Strain Energy for Material under Hydrostatic Pressure

We now proceed to evaluate the Strain Energy function defined in (16) in terms of the constants c_{11}, C_{111}, etc., of the stress-free state, defined in (15). For this purpose, we first carry out the finite hydrostatic deformation of the medium by which a point (a, b, c) is moved over to a point (x_0, y_0, z_0) given by $x_0 = (1+\eta)a$, $y_0 = (1+\eta)b$, $z_0 = (1+\eta)c$ where

$$\eta = \frac{\partial u}{\partial a} = \frac{\partial v}{\partial b} = \frac{\partial w}{\partial c}$$

giving the magnitude of the compression as a change of length per unit initial length. The corresponding Jacobian is

$$\mathrm{J}_0 = \begin{pmatrix} 1+\eta & 0 & 0 \\ 0 & 1+\eta & 0 \\ 0 & 0 & 1+\eta \end{pmatrix}. \quad (17)$$

From the Murnaghan formulæ for strain and stress (7 and 11), we get the strain and stress matrices respectively as

$$\begin{pmatrix} \eta+\eta^2/2 & 0 & 0 \\ 0 & \eta+\eta^2/2 & 0 \\ 0 & 0 & \eta+\eta^2/2 \end{pmatrix} \quad (18)$$

$$\begin{pmatrix} \dfrac{\partial\phi}{\partial\eta_1} & 0 & 0 \\ \hline 1+\eta & & \\ 0 & \dfrac{\partial\phi}{\partial\eta_2} & 0 \\ & \hline 1+\eta & \\ 0 & 0 & \dfrac{\partial\phi}{\partial\eta_3} \\ & & \hline 1+\eta \end{pmatrix}. \tag{19}$$

Substitution of the strain matrix values (18) in the energy expression (15) gives us the energy due to the hydrostatic pressure alone. To obtain the energy for the initial strain *plus* the infinitesimal strain, we formulate the corresponding J. If as a result of this additional strain the point (x_0, y_0, z_0) moves over to (x, y, z), the most general relationship between them will be given by

$$\begin{aligned} x &= (1+\delta_1)\,x_0 + \delta_6 y_0 + \delta_5 z_0 \\ y &= \delta_6 x_0 + (1+\delta_2)\,y_0 + \delta_4 z_0 \\ z &= \delta_5 x_0 + \delta_4 y_0 + (1+\delta_3)\,z_0. \end{aligned} \tag{20}$$

The transformation $x_0 \rightarrow x$ being thus given by the Jacobian

$$\mathrm{J}_\delta = \begin{pmatrix} 1+\delta_1 & \delta_6 & \delta_5 \\ \delta_6 & 1+\delta_2 & \delta_4 \\ \delta_5 & \delta_4 & 1+\delta_3 \end{pmatrix}. \tag{21}$$

In formulating J_δ in this form with 6 components, we have assumed that the rotations are removed beforehand. Special cases such as that of a simple shear, superposed over a finite strain, would require the consideration of an unsymmetrical J. We will not, however, consider such a case here for the sake of simplicity.

Now substituting the values of $x_0 = (1+\eta)\,a$, etc., we finally get the transformation from the initial position a, b, c to the final position x, y, z as

$$x = \mathrm{J}a$$

where

$$\mathrm{J} = (1+\eta)\,\mathrm{J}_\delta. \tag{22}$$

Forming $\frac{1}{2}(\mathrm{J}^*\mathrm{J} - \mathrm{E}_3)$, we obtain the strain matrix for this entire deformation $\eta + \delta\eta$, as

$$\begin{pmatrix} \mathrm{R}+q^2\delta\eta_1 & q^2\delta\eta_6 & q^2\delta\eta_5 \\ q^2\delta\eta_6 & \mathrm{R}+q^2\delta\eta_2 & q^2\delta\eta_4 \\ q^2\delta\eta_5 & q^2\delta\eta_4 & \mathrm{R}+q^2\delta\eta_3 \end{pmatrix} \tag{23}$$

where $\mathbf{R} = \eta + \eta^2/2 =$ Initial strain, $q = 1 + \eta$

$$\delta\eta_1 = \delta_1 + \tfrac{1}{2}(\delta_1^2 + \delta_5^2 + \delta_6^2) \qquad \delta\eta_4 = \delta_4 + \tfrac{1}{2}(\delta_2\delta_4 + \delta_3\delta_4 + \delta_5\delta_6)$$
$$\delta\eta_2 = \delta_2 + \tfrac{1}{2}(\delta_2^2 + \delta_4^2 + \delta_6^2) \qquad \delta\eta_5 = \delta_5 + \tfrac{1}{2}(\delta_1\delta_5 + \delta_3\delta_5 + \delta_4\delta_6)$$
$$\delta\eta_3 = \delta_3 + \tfrac{1}{2}(\delta_3^2 + \delta_4^2 + \delta_5^2) \qquad \delta\eta_6 = \delta_6 + \tfrac{1}{2}(\delta_1\delta_6 + \delta_2\delta_6 + \delta_4\delta_5) \tag{24}$$

It should be noted here that we are maintaining the distinction between the δ matrix (21) which specifies the displacement, and the $\delta\eta$ matrix which is the strain matrix corresponding to the J_δ transformation. Further, while we have taken our additional deformation as infinitesimal, we are still keeping the square terms δ_1^2, etc., in the expression for $\delta\eta$. This is necessary because the energy of the infinitesimal deformation ϕ' will ultimately have terms up to squares and products of the displacement derivatives δ_1, δ_2, etc. If ϕ' contained only quadratic terms in the $\delta\eta$, it would have been wholly unnecessary to keep any square of the δ in the expression for $\delta\eta$. However, when an initial stress is present, ϕ' contains linear terms in the $\delta\eta$ which give rise to terms of the second degree in the δ's as is evident from (24). Hence we note the important point that, when an initial stress is present, even an infinitesimal strain thereon will have to be treated as a finite one only, no approximation being justifiable in the value for the strain element. After the energy expression is formed using the correct value of the strain component, terms higher than the second powers of the displacement derivatives could be neglected, to justify its classification as an infinitesimal deformation.

We can substitute the values of the strains from (23) to get the total energy. An equivalent, but somewhat simpler method would be to note that an increase of $\delta\eta$ from the 'η' state gives rise to an increase of $\Delta\eta = (1 + \eta)^2\,\delta\eta$ in all the elements of the strain matrix. Here $\Delta\eta$ is the increase in strain when the strain is measured with reference to the stress-free state, while $\delta\eta$ is measured from the state of finite strain η. As the energy expression (15) refers to the initial stress-free conditions, any increase of the energy due to an increment of $\Delta\eta$ in the strain, can be most simply got from the Taylor formula,

$$\phi(\eta + \Delta\eta) - \phi(\eta) = \sum \frac{\partial\phi}{\partial\eta_r} \cdot \Delta\eta_r + \frac{1}{2}\sum\sum \frac{\partial^2\phi}{\partial\eta_r\partial\eta_s}\,\Delta\eta_r\Delta\eta_s \tag{25}$$

neglecting higher powers of the $\Delta\eta$. This is the energy of the infinitesimal deformation when referred to a unit volume of the stress-free state. We

multiply it by $1/\mathrm{Det}\,J_0$ to refer it to a unit volume of the 'η' state [*see* equation (12) in this connection], *i.e.*, by a factor $(1+\eta)^{-3}$. According to the energy method explained earlier, we equate this quantity to ϕ' to get

$$\begin{aligned}(1+\eta)^{-3}\,[\{&R\,(c_{11}+2c_{12})+R^2\,(3C_{111}+6C_{112}+C_{123})\}\\ &\times(1+\eta)^2\,(\delta\eta_1+\delta\eta_2+\delta\eta_3)\\ &+\tfrac{1}{2}\{c_{11}+R\,(6C_{111}+4C_{112})\}\,(1+\eta)^4\,(\delta\eta_1{}^2+\delta\eta_2{}^2+\delta\eta_3{}^2)\\ &+\{c_{12}+R.C_{123}+R.4C_{112}\}\,(1+\eta)^4\,(\delta\eta_1\delta\eta_2+\delta\eta_2\delta\eta_3+\delta\eta_3\delta\eta_1)\\ &+\tfrac{1}{2}\{4c_{44}+R\,(2C_{144}+4C_{155})\}\,(1+\eta)^4\,(\delta\eta_4{}^2+\delta\eta_5{}^2+\delta\eta_6{}^2)]\\ =\phi'=-P\,&(\delta\eta_1+\delta\eta_2+\delta\eta_3)+\frac{b_{11}}{2}\,(\delta\eta_1{}^2+\delta\eta_2{}^2+\delta\eta_3{}^2)\\ &+b_{12}\,(\delta\eta_1\delta\eta_2+\delta\eta_2\delta\eta_3+\delta\eta_3\delta\eta_1)\\ &+2b_{44}\,(\delta\eta_4{}^2+\delta\eta_5{}^2+\delta\eta_6{}^2). \qquad (26)\end{aligned}$$

Equating the coefficient of $\delta\eta_1$ on either side, we immediately get

$$-P=(c_{11}+2c_{12})\,\frac{\eta+\eta^2/2}{1+\eta}+\frac{(\eta+\eta^2/2)^2}{1+\eta}\,(3C_{111}+6C_{112}+C_{123})$$

which, on development in powers of η and retaining up to η^2, becomes

$$-P=\eta\,(c_{11}+2c_{12})+\eta^2\left(3C_{111}+6C_{112}+C_{123}-\frac{c_{11}}{2}-c_{12}\right). \qquad (27)$$

In the same manner by equating coefficients of $\delta\eta_1{}^2$, $\delta\eta_1\delta\eta_2$ and $\delta\eta_4{}^2$ we get

$$b_{11}=c_{11}+\eta\,(c_{11}+6C_{111}+4C_{112})+\eta^2\,(9C_{111}+6C_{112}) \qquad (28)$$

$$b_{12}=c_{12}+\eta\,(c_{12}+4C_{112}+C_{123})+\eta^2\left(6C_{112}+\frac{3}{2}\,C_{123}\right) \qquad (29)$$

$$b_{44}=c_{44}+\eta\left(c_{44}+\frac{C_{144}}{2}+C_{155}\right)+\eta^2\left(\frac{3}{4}\,C_{144}+\frac{3}{2}\,C_{155}\right). \qquad (30)$$

5. Effective Elastic Energy and Effective Elastic Constants

So far our task has been to derive an expression for the additional strain energy due to an infinitesimal deformation in powers of the strain components $\delta\eta$, each of which however involved not only terms linear in the δ_1, δ_2, etc., but quadratic terms in them as well. For further discussion on the elastic behaviour of the substance from the 'η' state, it will be necessary to express this energy in terms of $\delta_1 \cdots \delta_6$. Substituting from (24) in (16) and retaining terms up to the second power of δ's only, we get

$$\phi' = -\mathrm{P}(\delta_1 + \delta_2 + \delta_3) + \tfrac{1}{2}(b_{11} - \mathrm{P})(\delta_1^2 + \delta_2^2 + \delta_3^2) + b_{12}(\delta_1\delta_2 + \delta_2\delta_3 + \delta_3\delta_1) + (2b_{44} - \mathrm{P})(\delta_4^2 + \delta_5^2 + \delta_6^2). \tag{31}$$

The expression ϕ' refers to the total deformation energy which should be rendered available from external sources in order that the deformation η to $\eta + \delta\eta$ could be effected on a unit volume element in the η state. It has to be remembered however that an external force, namely the hydrostatic stress, is already present and there is the potential energy associated with this force. When displacements resulting in deformations δ_1, δ_2, δ_3 take place, an amount of energy $\Delta W = -\mathrm{P}(\delta_1 + \delta_2 + \delta_3)$ is released from this external potential energy. In other words the work done by the existing external force in this displacement which is ΔW can go in, as increase in internal energy, *i.e.*, the strain energy, and thus meet the part of the total requirement ϕ'. Hence the extra energy, that should be made available in order that the deformation η to $\eta + \delta\eta$ may take place, is given by $\phi_e = \phi' - \Delta W$. ϕ_e, which is the effective elastic energy, represents the energy associated with an infinitesimal deformation which takes place from a state of finite strain, just as the usual elastic energy ϕ refers to a similar deformation of a state with zero initial strain. ϕ_e is thus obtained from ϕ' by the removal of the linear terms $-\mathrm{P}(\delta_1 + \delta_2 + \delta_3)$. We have

$$\phi_e = \phi' - \Delta W = \phi' + \mathrm{P}(\delta_1 + \delta_2 + \delta_3) = \frac{c'_{11}}{2}(\delta_1^2 + \delta_2^2 + \delta_3^2) + c'_{12}(\delta_1\delta_2 + \delta_2\delta_3 + \delta_3\delta_1) + 2c'_{44}(\delta_4^2 + \delta_5^2 + \delta_6^2) \tag{32}$$

where

$$c'_{11} = b_{11} - \mathrm{P} = c_{11} + \eta(2c_{11} + 2c_{12} + 6\mathrm{C}_{111} + 4\mathrm{C}_{112}) + \eta^2\left(12\mathrm{C}_{111} + 12\mathrm{C}_{112} + \mathrm{C}_{123} - \frac{c_{11}}{2} - c_{12}\right)$$

$$c'_{12} = b_{12} = c_{12} + \eta(c_{12} + 4\mathrm{C}_{112} + \mathrm{C}_{123}) + \eta^2\left(6\mathrm{C}_{112} + \frac{3}{2}\mathrm{C}_{123}\right)$$

$$c'_{44} = b_{44} - \frac{\mathrm{P}}{2} = c_{44} + \eta\left(\frac{c_{11}}{2} + c_{12} + c_{44} + \frac{\mathrm{C}_{144}}{2} + \mathrm{C}_{155}\right) + \eta^2\left(\frac{3}{2}\mathrm{C}_{111} + 3\mathrm{C}_{112} + \frac{\mathrm{C}_{123}}{2} + \frac{3}{4}\mathrm{C}_{144} + \frac{3}{2}\mathrm{C}_{155} - \frac{c_{11}}{4} - \frac{c_{12}}{2}\right). \tag{33}$$

The new constants c'_{11}, c'_{12}, c'_{44} will be called the effective elastic constants. While ϕ_e could have been directly derived by substitution of relations such as $\delta\eta_1 = \delta_1 + \frac{1}{2}(\delta_1^2 + \delta_5^2 + \delta_6^2)$, in the function ϕ, the development of an intermediate function ϕ' as has been done in this paper helps us to retain $\delta\eta$ as it is, till a convenient stage is reached, whereafter ϕ_e could be easily deduced. This reduces the labour involved in a full substitution of $\delta\eta$ from the beginning itself.

The δ_1, δ_2 ... δ_6 are the displacement derivatives. In the infinitesimal theory, they are directly identified with the infinitesimal strain components themselves. We can therefore get the stresses required for effecting the δ deformation by the usual processes of differentiating the appropriate strain energy function, which in this case is ϕ_e. We thus obtain for the additional strains t_1, t_2 ... t_6 the relations

$$t_1 = c'_{11}\delta_1 + c'_{12}(\delta_2 + \delta_3) \tag{34}$$

with similar equations for t_2 and t_3 and

$$t_4 = 2c'_{44}\delta_4 \tag{35}$$

with similar equations for t_5 and t_6. (34) and (35) are indicative of the linear relationships which connect the additional stresses with the additional strains through the effective elastic constants c'_{11}, c'_{12}, c'_{44}.

6. Derivation of Effective Elastic Constants from Stress Matrix Method

In the foregoing sections we have indicated the derivation of the effective elastic energy and the effective constants from the energy method. It is also possible to derive the same from the stress matrix and this method has been adopted by some workers (Birch, 1947; Hughes and Kelly, 1953). The method is not simpler, since in any case, the energy function has to be evaluated as an essential step for the derivation of the stress from the Murnaghan formula $\mathbf{T} = (\rho_x/\rho_a)\,\mathbf{J}\,(\partial\phi/\partial\eta)\,\mathbf{J}^*$. We form the appropriate matrices for an $(\eta + \delta)$ transformation, and after the product matrix of all the three matrices J, $\partial\phi/\partial\eta$, $\mathbf{J}^*$ is worked out and the same is multiplied by ρ_x/ρ_a, we retain only the constant and terms linear in the δ's. This gives the total stress appropriate to an $\eta + \delta$ deformation. From this, the extra stress appropriate to the infinitesimal deformation has to be found out. A direct subtraction like $\mathbf{T}_{\eta+\delta} - \mathbf{T}_\eta$ to obtain the extra stress is incorrect, since the stress, being referred to the final state, has different reference conditions for $\mathbf{T}_{\eta+\delta}$ and $\mathbf{T}_\eta$ (which is really the pressure P in our present case). In this respect the position is more complicated than in the energy method. Whereas

$\phi(\eta+\delta)-\phi(\eta)$ employed in our energy method is an allowed subtraction as both refer to the common condition of a state of zero stress, $T_{\eta+\delta}-T_{\eta}$ in the stress matrix method is not an allowed subtraction in view of the difference in the reference frames. We have to refer $T_{\eta+\delta}$ and T_{η} to common reference conditions and then deduct the effect of the pressure. Birch calculated the total stress $T_{11}=T_1$ and equated it to an expression $-P+c'_{11}\delta_1+c'_{12}(\delta_2+\delta_3)$, wherein he identified c'_{11}, c'_{12}, etc., with the effective elastic constants. However, they would be so only if $T_{11}+P$ (it has to appear in this form as T_{11} is negative while P is kept positive) represents the extra pressure. But as pointed out earlier, the removal of the pressure term in this manner from T_{11} is not justified. Likewise he calculated T_{12} and on the basis that there is no initial shearing stress he identified T_{12} with $2c'_{44}\delta_6$. Here again, he has not taken into account the fact that a pressure P in an η state is equivalent to a stress tensor of a somewhat different type when referred to the $\eta+\delta$ state; the representation of the pressure in the $\eta+\delta$ state has in fact a component $-P\delta_6$ in the $T_6=T_{12}$ term, and $-P(1-\delta_2-\delta_3)$ in the T_{11} term as will be shown in the next paragraph. So, as long as the Murnaghan formulæ for stress, which refer everything to the final state, are employed, the pressure should also be referred to those final conditions, and to obtain the excess stress we have to subtract $-P(1-\delta_2-\delta_3)$ from T_{11} and similarly subtract $-P\delta_6$ from T_{12}. As the correction does not involve δ_1, c'_{11} is unaffected and it follows that c'_{11} as derived by us should be identical with that obtained by Birch. As the δ_2 term in T_{11} now comes with an additional correction $-P\delta_2$, the value of c'_{12} obtained by Birch will have to be corrected by subtracting P. Likewise, c'_{44} obtained by him should be corrected by the addition of P/2. We give below the values obtained by Birch which were developed up to the first power of η along with our values up to the same power, although in the actual working given by us earlier, we have developed up to η^2.

Values of Birch	Values obtained by authors
$c'_{11}=c_{11}+\eta(2c_{11}+2c_{12}+6C_{111}+4C_{112})$	$c'_{11}=c_{11}+\eta(2c_{11}+2c_{12}+6C_{111}+4C_{111})$
$c'_{12}=c_{12}+\eta(C_{123}+4C_{112}-c_{11}-c_{12})$	$c'_{12}=c_{12}+\eta(C_{123}+4C_{112}+c_{12})$
$c_{44}'=c_{44}+\eta\left(c_{44}+c_{11}+2c_{12}+\frac{C_{144}}{2}+C_{155}\right)$	$c'_{44}=c_{44}+\eta\left(\frac{c_{11}}{2}+c_{12}+c_{44}+\frac{C_{144}}{2}+C_{155}\right)$
$-P=\eta(c_{11}+2c_{12})$	$-P=\eta(c_{11}+2c_{12})$

The value of P when referred to the final $\eta + \delta$ conditions can also be obtained by using the formula given by Murnaghan $T^a dS^a = T dS^x$ where T^a is the stress in an initial frame with a surface area element given by dS^a, T the stress in the final state with an element of area dS^x. The relation between dS^x and dS^a is

$$dS^x = \frac{\rho_a}{\rho_x} (J^*)^{-1} \, dS^a. \tag{37}$$

Hence we get

$$T^a = \frac{\rho_a}{\rho_x} T \, (J^*)^{-1},$$

or

$$T = \frac{\rho_x}{\rho_a} T^a J^*. \tag{38}$$

In our case, the η state is the initial state and the $\eta + \delta$ state is the final state.

Hence

$$J = J^* = \begin{vmatrix} 1 + \delta_1 & \delta_6 & \delta_5 \\ \delta_6 & 1 + \delta_2 & \delta_4 \\ \delta_5 & \delta_4 & 1 + \delta_3 \end{vmatrix}$$

and

$$\frac{\rho_x}{\rho_a} = \frac{1}{\text{det. } J}.$$

Substituting these values, we find that the stress $-$ P in the η state appears, in the $\eta + \delta$ state, as the stress given by the matrix

$$\begin{pmatrix} -P(1-\delta_2-\delta_3) & -P\delta_6 & -P\delta_5 \\ -P\delta_6 & -P(1-\delta_3-\delta_1) & -P\delta_4 \\ -P\delta_5 & -P\delta_4 & -P(1-\delta_1-\delta_2) \end{pmatrix}. \tag{39}$$

Hence these matrix elements have to be subtracted from T_{11}, T_{12}, etc., before the correct extra stress is obtained.

Instead of referring P to the final $\eta + \delta$ state and removing its effect from T_{11}, T_{12}, etc., one could also refer the total stresses T_{11}, T_{12}, etc., to the η state and then remove P directly. This will not involve any modification of the pressure, whereas the stresses, since they are referred to the η state as the initial state, can be deduced from the simpler formula $T^a =$

$J(\partial\phi/\partial\eta)$. Here T^a is what Murnaghan (1951) calls the modified stress matrix. It can be verified that results identical with the above are obtainable by such a procedure as well.

7. DISCUSSION OF RESULTS

Experimental data concerning the third order constants are very meagre. Whatever is available [Hearmon (1953), Hughes and Kelly (1953)] suggests that all these constants are negative and an order of magnitude larger than the second order constants. In the discussion given by Hearmon (1953), the data obtained by Lazarus (1949) concerning c'_{ik} in respect of the cubic crystals KCl, NaCl, CuZn, up to hydrostatic pressures of 10,000 bars were considered. Hearmon plotted the ratio c'_{ik}/c_{ik} against η and obtained a nearly straight line relationship. Using the values of the slopes of these lines, he derived values for the 3 third order combinations C_a, C_b, C_d given by

$$C_a = 6C_{111} + 4C_{112}; \quad C_b = C_{123} + 4C_{112}; \quad C_d = \tfrac{1}{2}C_{144} + C_{155}.$$

In NaCl, for example, C_a was -100, C_b was -14 and C_d was -11, in units of 10^{11} dynes per sq.cm. The corresponding values of the second order elastic constants are roughly $c_{11} = 4{\cdot}9$, $c_{12} = 1{\cdot}2$, $c_{44} = 1{\cdot}2$. In view of the method employed, Hearmon has cautioned that the accuracy of these values is not likely to be high. However, the order of magnitude of the third order constants suggested by these calculations seems to be correct, and further work of Hughes and Kelly (1953) supports this view.

As the readings were taken in a portion of the $(c'_{ik}/c_{ik}, \eta)$ graph which was nearly straight, it is clear that, in this region the η^2 term in the formulæ (33) could be neglected. For the same reason, there would not be any appreciable difference whether Birch's expressions of the effective elastic constants, or those derived by us from the energy expression method are used. When, however, we use the values of the third order constants as derived above for discussing the behaviour of the energy function for large η, the η^2 term, as also the effective elastic constants as derived by us from the energy function will have to be used.

Thus, neglecting the second order constants in comparison with the third order ones, we find from (33) that each of the effective elastic constants can be represented as,

$$c'_{ik} = c_{ik} + A\eta + B\eta^2 \qquad (40)$$

where A equals C_a, C_b or C_d respectively as defined earlier, and B is nearly equal to 2A in case of c'_{11} and 3/2 A in case of c'_{12} and more than 3/2 A in

case of c'_{44}. A is ordinarily negative and as η itself is negative for compression, the formula shows that the elastic constants should, as a rule, increase with increasing compression, so long as η is not too large. Such an increase is to be expected, since these elastic constants express the magnitude of energy required for deforming a substance which is already in a compressed state. As the compression increases, the energy required for compressing further should naturally increase indicating increasing resistance of the substance to further deformation. What is interesting, however, is that the formulæ (33) and (40) indicate the possibility that the elastic constants might increase up to a point only and then start decreasing. That this will happen, other factors remaining unchanged, when $1 + 3\eta = 0$ or $\eta = -0{\cdot}3$, in the case of c_{12} and when $\eta = -0{\cdot}25$ in the case of c_{11} and less than $-0{\cdot}3$ in the case of c'_{44} may be inferred by equating $(dc'_{ik}/d\eta)$ to zero. However $\eta = -0{\cdot}25$ to $-0{\cdot}3$ corresponds to a very large strain difficult of realisation in practice. Since a decrease of the elastic constants with increasing pressure is itself indicative of anomalous behaviour, we have to conclude that matter should be expected to behave in an abnormal manner when the magnitude of compression becomes as high as 0·25 to 0·3.

This of course is a purely qualitative conclusion, and the magnitude might well be somewhat different when we develop c'_{ik} to include η^3 terms also. Other physical conditions such as the temperature are bound to play an important part and these have not been considered.

8. Effective Elastic Energy in Normal Co-ordinates

We note that the function ϕ_e given by (32) is separable in the variables δ_4, δ_5, δ_6 but not in δ_1, δ_2, δ_3 because of cross-products. To discuss the behaviour of this function, it is necessary to make a 'normal co-ordinate transformation' so that each variable could be treated independently. We introduce new orthogonal variables given by

$$\theta_1 = \frac{1}{\sqrt{3}}(\delta_1 + \delta_2 + \delta_3)$$

$$\theta_2 = \frac{1}{\sqrt{2}}(\delta_1 - \delta_2)$$

$$\theta_3 = \frac{1}{\sqrt{6}}(\delta_1 + \delta_2 - 2\delta_3). \tag{41}$$

In terms of these, we rewrite (32) as

$$\phi_e = (c'_{11} + 2c'_{12})\frac{\theta_1^2}{2} + (c'_{11} - c'_{12})\frac{\theta_2^2 + \theta_3^2}{2} + 2c'_{44}(\delta_4^2 + \delta_5^2 + \delta_6^2). \tag{42}$$

The system will therefore become unstable when any of the coefficients $c'_{11} + 2c'_{12}$, $c'_{11} - c'_{12}$ or c'_{44} becomes negative. Of these, the first is only hypothetical, because c'_{11} and c'_{12} being initially positive, the term $c'_{11} - c'_{12}$ will, if at all, become negative long before $c_{11}' + 2c_{12}'$ does so and we may safely exclude the first case. As regards the other two coefficients $\frac{1}{2}(c'_{11} - c'_{12})$ and c'_{44}, we notice that both are identical in the isotropic case. For such a case, we may take the criterion that as soon as c'_{44} tends to assume negative values, instability sets in. With the present meagre available data, it is not possible to calculate the magnitude of the compression at which this phenomenon sets in for any particular case like the interior of the earth. However, the form of c'_{44} especially in its expression as $b_{44} - P/2$ suggests that with monotonously increasing pressure, the possibility of its becoming negative at some stage of the compression cannot be ruled out. This is especially so in substances in which c_{44} goes on decreasing with pressure such as in the case of KCl even from the very beginning (Hearmon, 1953). Even if c_{44} increases at first and decreases later due to the importance of the η^2 term, or decreases due to other causes such as the effect of temperature, a stage will be reached when c'_{44} becomes negative. It is obvious that the substance then becomes unstable under the action of shearing stresses and this may be interpreted by saying that it can no longer sustain shear waves.

A more detailed discussion of the instability problem, and the extension of the present work to include a finite initial stress of any type, will be taken up in subsequent papers.

9. SUMMARY

In order to study the elastic behaviour of matter when subjected to very large pressures, such as occur for example in the interior of the earth, and to provide an explanation for phenomena like earthquakes, it is essential to be able to calculate the values of the elastic constants of a substance under a state of large initial stress in terms of the elastic constants of a natural or stress-free state. An attempt has been made in this paper to derive expressions for these quantities for a substance of cubic symmetry on the basis of non-linear theory of elasticity and including up to cubic powers of the strain components in the strain energy function. A simple method of deriving them directly from the energy function itself has been indicated for any general case and the same has been applied to the case of hydrostatic compression. The notion of an effective elastic energy—the energy required to effect an infinitesimal deformation over a state of finite strain—has been introduced, the coefficients in this expression being the effective

elastic constants. A separation of this effective energy function into normal co-ordinates has been given for the particular case of cubic symmetry and it has been pointed out, that when any of such coefficients in this normal form becomes negative, elastic instability will set in, with associated release of energy.

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THE RAMAN SPECTRA OF POLYCRYSTALLINE SOLIDS

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1. Introduction

Crystalline solids as found in nature or prepared artificially usually appear as polycrystalline masses, large and well-developed crystals being the exception rather than the rule. In the study of the Raman effect, it is often necessary to make use of such material. The internal reflections within the solid and the parasitic illumination resulting therefrom create difficulties in the successful recording of the spectra. These difficulties are enormously enhanced when, as is often the case with artificially prepared material, the solid appears in the form of very fine particles which are non-adherent or only loosely adherent to each other. The special techniques necessary to obtain any useful results with such material have been the subject of numerous investigations in the past, reference to which will be made later in the paper.

In the present author's studies on the Raman spectra of crystals, extensive use has been made by him of the λ 2536·5 resonance radiation of the mercury arc and of the special technique originally proposed by Rasetti in that connection. It appeared to him therefore to be of interest to explore the possibility of using the same technique for satisfactorily recording the Raman spectra both of polycrystalline solids and of the finest crystal powders. The present paper is of a preliminary nature. It discusses the problems which arise in this connection and presents the results obtained in a few typical cases of interest.

2. A Survey of the Problem

The theory of the propagation of light in polycrystalline media developed by C. V. Raman and K. S. Viswanathan (1955) and discussed by C. V. Raman (1957) with reference to the facts of observation provides an insight into the behaviour of these substances with regard also to the diffusion of light in them, since the properties in relation to transmission and diffusion of light are complementary to each other. The following points are germane to our discussion here on the nature and origin of the parasitic scattering and how

best it can be minimized. When the sizes of the crystallites are large compared with the wavelength of light and the birefringence of the solid is appreciable, the effects arising may be considered from the standpoint of geometrical optics as reflection and refraction of the incident light at the intercrystalline boundaries. Since for a finite volume of the sample the total area of the boundaries which scatter increases with diminishing particle size, the parasitic scattering of light would naturally be greater in the case of finer particles, and a very small thickness of the medium suffices therefore to diffuse the incident light totally in directions backward. However, as the size of the crystallites diminishes further and becomes comparable to that of the wavelength of light the effects arising have to be considered from the point of view of wave-optics. In the case of a weakly birefringent solid the diminution in the particle size at such a stage should result in a diminution in the scattering and hence correspondingly increased transmission.

The foregoing remarks have a bearing on the case of fine crystal powders. Since the intensity of the diffusion of light at the boundaries of the crystallites depends on the refractive index of the substance with reference to the medium surrounding it, the immersion of the powder sample in a medium of nearly equal index should considerably reduce the parasitic scattering. The technique of forming pellets of the substance diluted in a solid medium of nearly equal index as is done for infra-red studies may also be effective in reducing the parasitic scattering. Finally, the use of particles of colloidal dimensions should also be helpful in such studies.

We shall, in the following, consider the effects arising from the parasitic illumination and how the earlier investigators tried to minimize it. The parasitic scattering besides causing an intense halation close to the exciting line produces a general fog over the entire region of the photographic plate, the latter effect arising from the multiple reflections of the light by the optics within the spectrograph. In addition, the continuous spectrum that is invariably present even in low pressure arcs is also recorded strongly. As a result, not only does it become impossible to observe any Raman lines in the vicinity of the exciting radiation, but also weak Raman lines of even high-frequency shifts are masked by the general background of illumination. Apart from all this, the imperfect transparency of the specimens themselves (resulting from their polycrystalline nature) causes only a very small depth of the substance to be effectively operative for observing the Raman scattering.

One of the important advances made in the study of the Raman spectra of crystal powders is due to R. Ananthakrishnan (1937) who developed what is known as the technique of complementary filters. A concentrated solution of iodine in carbon tetrachloride was interposed in the path of the incident

radiation to absorb all the visible mercury lines excepting that at λ 4046. The scattered light was filtered through a strong solution of sodium nitrite to absorb the exciting radiation λ 4046. By this procedure he was able to obtain fairly clear spectra exhibiting the high-frequency Raman lines; however, since the absorption of the $NaNO_2$ solution extended over a finite region on either side of λ 4046, the low-frequency lines could not be recorded. A similar technique was also developed by him for use with λ 4358 excitation. Another technique used with success was due to Billroth, Kohlrausch and Reitz (1937) who constructed a special spectrograph consisting of two parts, each with a prism and two lenses and with a common slit between them. The light was incident on a plate on which was spread the crystal powder. This plate was set at such an angle so that its position was conjugate to the position of the photographic plate on which the lines were recorded. In effect, the lines of different wavelengths recorded on the photographic plate emanate from different corresponding points on the former plate on which the powder is deposited. By screening off the point on the plate from which the radiations λ 4358 emanate, the overexposure arising due to this line was greatly reduced. Apart from such methods, absorption and interference filters have also been used to monochromatize the incident radiation and for removing the continuous background close to the exciting line. P. Krishnamurti (1930) used low-pressure arcs which had only a weak continuum and removed even this by a filter of didymium chloride solution. J. Brandmuller (1953) and M. C. Tobin (1959) have employed interference filters for monochromatizing the incident readiation, as also for suppressing the exciting radiation attendant with the Raman scattering.

Though with the aid of the above techniques it is possible to record the strong lines in the high-frequency region of the spectrum, the recording of the lattice frequencies which are of much interest in the case of studies on crystals is still a difficult problem. This is due to the fact that the absorption characteristics of all known filters extend over a finite range on either side of the exciting radiation that they are intended to suppress. On the other hand, the use of interference filters require that parallel light be employed, with the consequence that the scattered beam that can be brought to a focus on the slit of the spectrograph is of considerably reduced intensity. In addition, the low scattering power in the visible region of the spectrum coupled with the fact that only a small depth of the substance is effectively available for observation of the Raman scattering makes it very difficult to record weak Raman lines. It is in these respects that the technique of excitation of the Raman effect with the λ 2536·5 radiation, which we shall discuss in the following section, proves to be advantageous.

3. The Rasetti Technique

The details of this technique which have been fully described in an earlier paper by the author (1957) consist mainly of (i) the use of the intense λ 2536·5 resonance radiation emitted by a water-cooled magnet-cotrolled quartz mercury arc and (ii) the suppression of the parasitic illumination of λ 2536·5 radiation attendant with the Raman scattering by a filter of mercury vapour inside the spectrograph. The principal advantages in the technique arise from (i) the exceptional intensity of the exciting line compared to the neighbouring lines of the spectrum, (ii) the increased scattering power in the ultraviolet region of the spectrum and (iii) the successful elimination of the exciting radiation from the scattered light, thereby enabling the observation of the lattice lines appearing close to it. The power of the technique can be gauged by comparing the results of two studies by the author (1956, 1957) on magnesite and calcite. Whereas with the former and using the visible radiations of the mercury arc, only five lines could be observed with difficulty, in the latter no less than thirty-three frequency shifts could be clearly recorded. Apart from studies with single crystals, this technique has also been employed by the author (1959) to record the Raman spectra of several solid hydroxides, most of which were available either in the form of polycrystalline masses or as fine powders. It had been noticed that, though the strong Raman lines could be easily recorded, the continuous spectrum accompanying the exciting radiation impedes the observation of weaker Raman lines. Monochromatization of the incident beam, it is hoped, would help in the recording of the weaker lines also.

4. The Present Study: Its Results and Discussion

In the present study, we have considered two classes of substances, *viz.*, fine powders and compact polycrystalline solids. While in the former the crystallites are only loosely adherent to each other, in the latter the different microcrystalline domains of the substance are either linked together by atomic and intermolecular forces or held together by a cementing medium to form a compact solid. Besides the general interest attached to studies on the Raman spectra of such materials, there arise the important questions whether their Raman spectra would exhibit any variations depending on the size of the crystallites, and if so how small they have to be before such effects can be observed.

Calcite was chosen as a typical case for the exploratory studies on fine powders since its Raman spectrum is very well known. Two samples of $CaCO_3$ were used to record the spectra. One of them was the readily available commercial powder which contained aragonite as well. The method of

sedimentation was used both to obtain a powder of uniform particle size and also to remove the aragonite—which being denser than calcite settles at a fast rate. The other sample used was calcite precipitated in the cold by the addition of solutions of $CaCl_2$ and K_2CO_3. The powder was deposited thinly on the inside of a glass bulb which had two windows cut out for incident and scattered radiations. The spherical form of the bulb served to effectively utilize the exciting radiation by multiple reflections inside the container. The size of the particles of the powder used to record the spectrum was about 1 μ and was estimated under a high-power microscope. The spherical bulb was kept jammed against a water-cooled magnet-controlled quartz mercury arc intensely emitting the λ 2536·5 resonance radiation and the scattered light was focussed on the slit of the spectrograph by a quartz condenser.

Plate II accompanying this paper reproduces the microphotometer record of the Raman spectrum. The frequency shifts observed therein, *viz.*, 1086, 282 and 155 cm.$^{-1}$ are fairly sharp and are identical with the frequency shifts recorded with large crystals of calcite. The spectrum does not exhibit any alteration either in the frequency shifts or their widths. Besides the above three lines, it should have been possible to record two other weaker lines at 712 and 1436 cm.$^{-1}$ but for the fact of the continuous spectrum of the arc masking them.

As typical cases of polycrystalline solids, we have chosen alabaster wherein the crystallites are randomly orientated, and fascicular or columnar gypsum consisting of crystallites in the form of rods (the *b*-axes of the crystallites being the axes of the rods) arranged parallel to each other. The X-ray diffraction pattern of the specimen of alabaster used in the present study had been reported earlier by C. V. Raman and A. Jayaraman (1954) and exhibits spotty rings indicating the random orientation of the crystallites in it, the particle sizes being of the order of 10 μ. In the case of fascicular gypsum the rods though of minute dimensions are easily visible. The X-ray diffraction patterns recorded for it show that whereas the *b*-axes are all parallel to each other, the *c* and *a* axes exhibit a limited range of variation. Owing to the low birefringence of gypsum, both the specimens were translucent and their spectra could therefore be recorded without much difficulty. The spectrum of a single crystal of selenite in the form of a rectangular tablet was also recorded for comparison. The exciting radiation was incident on the broad face of the crystal and the scattering observed along an edge (perpendicular to the *b*-axis). In the case of fascicular gypsum the exciting radiation was incident parallel to the *b*-axis and the scattering observed perpendicular thereto.

Figures (*b*), (*c*) and (*d*) in Plate I accompanying this paper reproduce the Raman spectra of selenite, fascicular gypsum and alabaster recorded with adequate intensity. Figures (*a*) and (*e*) show the spectrum of the mercury arc for comparison. It is evident that the spectra recorded in the three cases exhibit no differences with regard to either the positions or the widths of the lattice and internal frequency shifts. The only noticeable feature is a variation in the relative intensities of the two intense water-bands ; this feature is a well-known orientational effect arising from the fact of the water molecules in gypsum being arranged in layers perpendicular to the *b*-axis (*vide*, *e.g.*, Roop Kishore, 1942). Finally, it should be remarked that with the same specimens it would have been impossible to obtain such clear spectra exhibiting the lattice lines with the visible radiations of the mercury arc as exciters of the Raman effect.

That no differences arise from the polycrystalline nature of the solids as well as from the finely divided form of the powders is consistent with the fact that the ranges of interatomic and intermolecular forces in crystals do not extend beyond a few lattice spacings. The individual crystallites in the polycrystalline samples and the fine powder used in the present study are still too large—each containing an enormous number of unit cells, of the order of 10^{10}. Since the number of lattice cells located well within the crystallites is large compared with that of the number of cells near the surface, no significant effects such as an alteration in the value of the frequency shifts, their intensities or widths can be expected to arise.

5. Concluding Remarks

The present studies have clearly shown that the Rasetti technique can be successfully employed to investigate the Raman spectra of polycrystalline masses and fine powders. However, particularly in the case of fine powders the continuous spectrum in the arc masks the weaker Raman lines. It is hoped that the parasitic illumination can be reduced considerably by the following techniques, *viz.*, (i) monocnromatization of the incident beam, (ii) immersion of the powder in a liquid of nearly equal refractive index, (iii) by dilution of the sample in a substance of suitable refractive index and forming tablets of the substance under high pressure and (iv) use of powders of colloidal dimensions and dispersed as in method (ii) or (iii).

In conclusion, the author wishes to express his sincere thanks to Professor Sir C. V. Raman, F.R.S., N.L., for his keen interest in this investigation and for the helpful discussions he had with him.

6. SUMMARY

The paper discusses the experimental techniques with regard to the recording of the Raman spectra of polycrystalline solids. The present studies on the typical cases of polycrystalline gypsum, and calcite in the form of a finely divided powder show that the Rasetti technique can be successfully employed to obtain clear spectra of such substances and also indicate the scope for further improvements in the techniques. It emerges that the polycrystalline nature of the gypsum and the finely divided form of the powder studied have no observable influence on their spectra.

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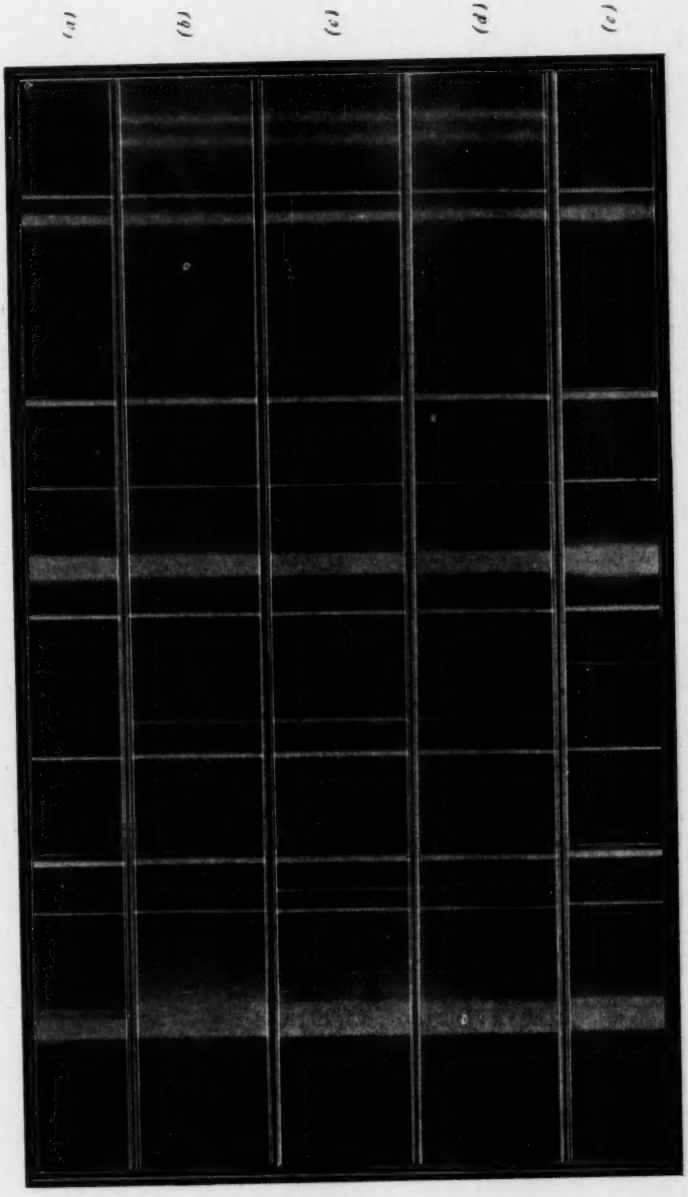

FIG. 1. The Raman spectra of various forms of gypsum: (*b*) Selenite; (*c*) Fascicular gypsum; (*d*) Alabaster. (*a*) and (*e*) Spectrum of the mercury arc.

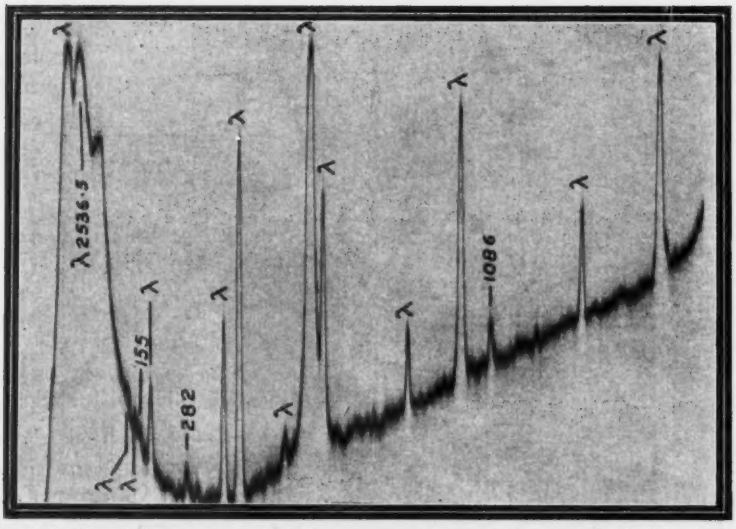

FIG. 2. The microphotometer record of the Raman spectrum of a fine powder of calcite (of particle size 1 μ).

A MODEL FOR HYPERFRAGMENTS*

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At the present time our knowledge on the structure of the nucleon-Λ hyperon interaction is quite poor since there are no direct measurements on $N - \Lambda$ scattering. That they interact strongly is inferred from the large production cross-section of strange particles and from the existence of hyperfragments which contain a bound Λ hyperon in a complex nucleus. There are several careful measurements on the properties of hyperfragments, especially on the binding energies[1]; hence it would be desirable to develop a systematic method of analysis which would relate the binding energies to the matrix elements of the $\Lambda - N$ interaction.

Meson theory suggests an extremely complex structure for this interaction. Since the Λ hyperon has spin $\frac{1}{2}$, the $\Lambda - N$ forces can be analysed in terms of triplet and singlet central forces, the spin orbit force, the tensor force and the quadratic spin-orbit force as in the $n - p$ system. But since the Λ hyperon is an isotopic singlet, Yukawa processes involving single pion emission by a Λ hyperon are not allowed ; consequently the asymptotic one-pion " tail " is absent here and the range of the $\Lambda - N$ forces is expected to be considerably shorter. Now the two-pion contribution to the potential is naturally more complicated and cannot be clearly separated from the one-kaon contribution. Also, at these short ranges it is no longer legitimate to treat the " actual " potential in terms of a $\Lambda - N$ system alone, since the reaction $\Lambda + N \rightarrow \Sigma + N$ is possible in addition to $\Lambda + N \rightarrow \Lambda + N$ and hence the interaction is better described in terms of a " potential matrix " for the hyperon-nucleon system ; and the off-diagonal terms of this potential matrix have a long range associated with a one-pion tail.

In contrast to this complexity the properties of hyperfragments would depend only on some average properties of the interaction ; a parallel instance is the dependence of low-energy scattering only on zero-energy scattering

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length and effective range. Of course, one may attempt[2] to solve the Schrödinger equation for the many-particle system using an associated interaction structure with unknown parameters, but this method requires for its practical implementation, some approximation technique like the variational method ; and even then, except for the simplest systems, to make the calculation practicable one has to invoke special models. We have a parallel instance in the theory of complex nuclei, but here the shell model has been a good first approximation to nuclear structure, at least as far as nuclear low-lying levels are concerned. Since one has to use a model anyway, it becomes interesting to see if it can be patterned after the theory of complex nuclei.

We have investigated this problem[3, 4] and developed in detail a model for hyperfragments. The physical postulates are that the system is well represented by a suitably antisymmetrized product of one-particle wave functions with two-particle interactions. We also make the assumption of $j-j$ coupling so that the one-particle wave functions may be classified as $S_{1/2}$, $P_{3/2}$, $P_{1/2}$, $D_{5/2}$, etc. The hyperon is always in the $S_{1/2}$ state at least for the low-lying states ; and all hyperfragments that have so far been identified correspond to nuclei belonging to the $S_{1/2}$ and $P_{3/2}$ shells. The two-particle interactions are assumed to lead to negligible configuration mixing so that the low-lying levels are almost pure configurations ; this assumption is certainly more accurate for the energy eigen values than for the wave functions themselves. In the absence of inter-particle forces the ground state of the model is many fold degenerate, but the interactions split this ; and the low-lying levels of the model with interactions are all obtained from this level ; they all hence correspond to the same set of one-particle configurations coupled in different fashions.

Having specified the model, one could proceed to calculate the energy levels in terms of the two-body interaction parameters. Since the nucleon binding energies are known, we shall take advantage of this to subtract out the ground state energy of the nucleon group ; since the $\Lambda - N$ interaction is somewhat weaker than the $N - N$ interaction for the first excited states of the hyperfragments, the nucleon group is in its ground state. In any case this is true of the ground state ; and for S-shell nuclei there are no bound excited states anyway. This restriction to hyperfragment states with unexcited nucleon groups permit us to label these states simply by the two spins which in general have two values corresponding to the parallel and the antiparallel spin orientations of the Λ and the spin of the nucleon group.

In the actual calculations, the so-called "Projection Theorem"[5] furnishes a powerful tool, in that it relates in our model, the matrix

elements of two-particle operators like the interaction energy for the many-particle wave functions in terms of the simpler matrix elements for two-particle configurations and coefficient of fractional parentage. The method is now useful in those cases where the expression in terms of the fractional parentage coefficients have a summable form so that closed expressions result. Fortunately all the hyperfragments that we discuss have this structure and so one can work with these closed expressions. The details and derivations may be found elsewhere.

There are four S-shell hyperfragments which have been identified ${}_{\Lambda}He^{3}$, ${}_{\Lambda}H^{4}$, ${}_{\Lambda}He^{4}$, ${}_{\Lambda}He^{5}$. The first and last are isotopic singlets and the other two form a doublet ; they correspond to the deuteron, the triton, He^{3} and the alpha particle. The experimental[1] values for the binding energies are respectively 0·12 Mev., 2·20 Mev., 2·36 Mev. and 3·08 Mev. There are three parameters[3] occurring in the expression for the Λ-binding energy, namely, the one-particle energy of the hyperon (T_{Λ}) and the singlet and triplet matrix elements (S_0, S_1) of the (charge-independent) $N - \Lambda$ interaction for the configuration $S_{1/2}\,S_{1/2}$. The possible spin assignments and theoretical expressions for the binding energies in terms of these parameters deduced from the binding energies for the antiparallel spins are $T_{\Lambda} = 8{\cdot}28$ Mev., $S_0 = -4{\cdot}88$ Mev., $S_1 = -2{\cdot}16$ Mev. While charge independence demands that ${}_{\Lambda}H^{4}$ and ${}_{\Lambda}He^{4}$ should give the same binding energy, experiments give different values agreeing within experimental error ; in computing the parameters for the model, we have averaged over these two values. For the parallel spin configuration the model parameters cannot be found since one notices from Table I that the expressions for the binding energies form a degenerate set which is inconsistent with the experimental values. This data thus indicates antiparallel configuration of the hyperon spin and the spin of the nucleon group and in particular demands that ${}_{\Lambda}He^{4}$ has spin 0. This last result is particularly important since the large rate of the reaction $K^{-} + He^{4} \rightarrow {}_{\Lambda}H^{4} + \pi^{-}$ then argues for a pseudoscalar kaon.[2] This large rate makes it irrelevant to know if there is a loosely bound excited state[6] of spin 1 for ${}_{\Lambda}He^{4}$; but from the parameters deduced above and the expressions for the binding energies, according to Table I, one finds that there are no bound excited states for any of the S-shell hyperfragments. One also notices that the $\Lambda - N$ interaction is definitely spin-dependent and attractive and the ratio $S_0/S_1 \sim 2$ is consistent with the previous estimates by Dalitz and Downs.[7] It turns out that the systems $nn\Lambda$ and ${}_{\Lambda}He^{3}$ are unbound.

A similar analysis can be carried through for P-shell hyperfragments. There are thirteen hyper nuclides belonging to the $P_{3/2}$-shell and among them there are a sufficiently large number of events[1] on four (${}_{\Lambda}Li^{7}$, ${}_{\Lambda}Li^{8}$, ${}_{\Lambda}Be^{9}$,

TABLE I

S-Shell Λ^- binding energy in terms of two-particle interaction parameters and the hyperfragment spin assignments

(A = 3, 4, 5)

Hyperfragment	J	Coefficients of		
		T_Λ	S_0	S_1
${}_\Lambda H^3$	$\frac{1}{2}$ (antiparallel)	1	3/2	$\frac{1}{2}$
	3/2 (parallel)	1	0	2
${}_\Lambda H^4$, ${}_\Lambda He^4$	0 (antiparallel)	1	3/2	3/2
	1 (parallel)	1	$\frac{1}{2}$	5/2
${}_\Lambda He^5$	$\frac{1}{2}$	1	1	3

${}_\Lambda Li^9$) and the parameters P_2', P_1', (defining the $\Lambda - N$ interaction for the configuration $S_{1/2}$, $P_{3/2}$ for states with J = 2, 1 respectively) are deduced from a least-squares fit to those. In this case it is advantageous to subtract the binding energy of the ${}_\Lambda He^5$ hyperfragment so that the one-particle contribution disappears. The analysis is too lengthy to be reproduced here but the comparison between theory and experiment for the binding energies is given in Table II. Using these parameters one can predict the first excited states of these hyperfragments and the binding energies of the other $P_{3/2}$-shell hyperfragments. A comparison of the latter prediction with experiment is given in Table III. One notices that while the fit is satisfactory, it is difficult to differentiate between the parallel and the anti-parallel configurations on the basis of binding energy data alone.

The same model may be applied to calculate other properties; for example one may develop a projection formula for the magnetic moments of hyperfragments,[4] but these do not appear to be amenable to immediate measurement. More useful would be a correlation of the decay dynamics. For mesic decay modes, especially in the lighter hyperfragments, pion rescattering corrections may be ignored in a first approximation; and it is then possible to write the weak decay interaction as a two-particle operator with the pion wave function treated as an "external" field; this calculation is quite analogous to the treatment of radiation processes in atomic systems to lowest order.

TABLE II

Comparison between theory and experiment for the binding energies of $P_{3/2}$ shell hyperfragments (all energies given in Mev.)

Hyperfragment	"Reduced" Binding Energy	Theory	
		Anti-parallel spins	Parallel spins
${}_{\Lambda}Li^{4}$	−2·38	−2·18	−2·10
${}_{\Lambda}Li^{8}$	−3·03	−3·16	−3·14
${}_{\Lambda}Be^{9}$	−3·52	−3·49	−3·53
${}_{\Lambda}Li^{9}$	−4·12	−4·14	−4·19

TABLE III

Predicted and measured binding energies for rare P-shell hyper fragments

Hyperfragment	Experiment	Theory	
		Antiparallel	Parallel
${}_{\Lambda}He^{7}$	3·0 ·7	4·73	4·84
${}_{\Lambda}Be^{8}$	6·6 ·6	6·24	6·22
${}_{\Lambda}Be^{11}$	9·9 ·6	9·18	9·37
${}_{\Lambda}Be^{12}$	9·8 ·6	9·73	9·75
${}_{\Lambda}C^{13}$	10·8 ·6	10·10	10·10

For non-mesic decays also one can (to a poorer approximation) use a two-particle decay operator. These calculations are now being completed, but our object in mentioning them is to point out that these are tests of the model independent of binding energy determinations, though there is no guarantee that the model should be adequate for decay processes ; again, the situation as far as beta and gamma transition matrix elements in complex nuclei furnishes a parallel.

One might at this point raise the question of the validity of a shell model with two-particle interactions only,[6] even as a first approximation in such a region of low mass numbers ; one may also point out that in the case of the $\Lambda - N$ interaction, the three body forces $N - \Lambda - N$ brought about by the exchange of a pion with each of the nucleons may be important.[2] With regard to these points one has to remember that in setting up the model one has tacitly assumed the existence of sufficiently bound configuration of the particles so that the possibility of finding a particle far from the rest of the nucleus is fairly small ; and a substantial part of the many-body forces (which are equally well present in ordinary nuclei) is already used up in setting up these one-particle eigen functions. In this sense, we are working not so much with two-particle interactions but rather with a two-particle correlation approximation. It is perhaps unfortunate that we are thus deprived of knowing the exact two-particle interaction, but then the interaction parameters that we find are the combinations relevant for the structure of the many-body system. The general effect of many-particle correlations is to prevent the two-particle interaction parameters from having any significant dependence on the two-body potential and has thus the same qualitative nature as the Pauli principle and the " hard " core ; in view of these we believe that the present model is a fair representation of the physical situation and that the interaction parameters are suitable averages of the true two-particle interaction in the neighbourhood of these average separation. We hope to develop these considerations in a more quantitative fashion so as to make more specific inferences about the $\Lambda - N$ potential.

However, a test of the degree of validity of the model for hyperfragments is suggested[8]: one could see how good is a similar model for the corresponding S and P shell nuclei. (Usually this region of atomic numbers is considered " off limits " for the shell-model !) We have three binding energies for the S-shell: the deuteron, triton He^3 and alpha particle. With a notation similar to that used for hyperfragments, we have

$$2T_N + S_1' = -2{\cdot}23 \text{ Mev.}$$

$$3T_N + \frac{3}{2}S_1' + \frac{3}{2}S_0' = -8{\cdot}49 \text{ Mev.}$$

$$4T_N + 3S_1' + 3S_0' = -28{\cdot}30 \text{ Mev.}$$

From which we get $T_N = +5{\cdot}67$ Mev., $S_1' = -13{\cdot}56$ Mev. and $S_0' = -3{\cdot}43$ Mev. Notice that the one-particle energy is smaller here (corresponding to a much stronger binding) as compared with the value obtained for T_Λ. If we now try to predict the virtual singlet level of the $n - p$ system we find

that its " excitation energy " is far too high ; it then appears that the model fails here. But the reason for the failure is easily found; in contrast to the triton and the alpha particle the deuteron is a rather " open " structure. The wave functions are spread out much farther than the one-particle wave functions appropriate to the S-shell. The residual two-particle interaction has of course the one-pion tail in this case and the spread out wave functions exploit this attractive tail and get further bound. If this explanation is physical, then the relation between the interaction parameters and the one-particle energy for the deuteron should contain a smaller energy ; if we put for this binding energy the value zero, we get an altered set of parameters and these bring the predicted singlet level nearer zero energy. It is still too high, but this must also happen since the unbound singlet level should obtain more " extra binding ". Similar studies have been made for the $P_{3/2}$ and shell nuclei also.[9, 10] And the fit to binding energies is to better than two per cent. The lesson of these studies is that for " compact " (sufficiently bound) nuclei the model is adequate.

This analysis now raises the question to what extent our predictions for the hyperfragments is modified by these " extraordinary " corrections ; this is especially important since ${}_{\Lambda}H^{3}$ is only loosely bound and one might see if these corrections could remove the inconsistency for one parallel spin configurations. One verifies immediately that for an attractive tail the corrections go in the wrong direction (since for consistency we need the binding energy of about 0·5 Mev.); on the other hand, a repulsive tail behaves in a very different manner from an attractive tail and is relatively unimportant for a one-particle wave function which was sufficiently compact to start with. For the P-shell hyperfragments all of the binding energies are considerably larger. It is to be emphasized that the corrections are qualitatively expected to be much less important since no long range tail for the Λ —N interaction is believed to exist ; and the one-particle wave function being an extended wave function (corresponding to the large positive value of T_{Λ}), the residual change in them is unimportant.

This, then, is our model. The main conclusions derived from this analysis are the spin dependence of the Λ — N interaction the zero spin of ${}_{\Lambda}He^{4}$ and the consequent odd parity of the Kaon ; and finally the comparative weakness of the Λ — N interaction and the consequent slowly varying extended wave function of the Λ^{-} hyperon. This last point is particularly relevant in connection with the omission of pion rescattering corrections in correlating the decay dynamics.

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We wish to thank Professor M. M. Block for discussions on the physics of hyperfragments ; Professor H. Feshbach for pointing out to us the test on S and P shell nuclei ; and Miss Fleur Wang for making available to us her calculations for the $P_{1/2}$ shell nuclei and for checking part of our calculation. Finally we wish to thank Professor Alladi Ramakrishnan for his interest in the preparation of this paper.

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THE DIRAC EQUATION FOR MANY-ELECTRON SYSTEMS

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1. Introduction

The well-known relativistic wave equation for an electron[1] was derived by Dirac by factorising a second order equation into two linear equations. It is the object of the present note to point out that the Dirac equation is simply the eigenvalue equation of the magnitude of the momentum four-vector, and that one can derive it by expressing the magnitude of the momentum vector in terms of its four components.

The above idea enables one to generalise the Dirac equation and obtain a relativistic equation for systems containing several electrons. In Section 3, we have given the wave equation (Equation 16) for a system composed of several particles and this is very similar in form to the Dirac equation. Relativistic wave equations for a system of two electrons have previously been given by Eddington,[2] Gaunt[3] and Breit[5] of which the one given by Breit is the most satisfactory. By replacing the velocities v^{I} and v^{II} of the electrons by the spin matrices $-ca^{I}$ and $-ca^{II}$ in a Hamiltonian given by Darwin,[4] Breit was able to obtain an approximate wave equation for two-electron systems. It is shown in Section 4, that Equation (16) leads to the Breit equation when it is represented in the product space of the two electrons.

2. The Momentum Four-Vector

Before proceeding further, we first state a result which was first proved by Weyl[6] for a vector in a n-dimensional space and which we shall apply presently.

(*a*) *Lemma.*—Let $(x_1, x_2, \ldots, x_n)$ be the co-ordinates of a vector $\vec{r}$ in an Eucledian space with reference to a system of orthogonal axes, and let $r = (x_1^2 + x_2^2 + \ldots + x_n^2)^{\frac{1}{2}}$ denote the 'magnitude' or 'length' of the vector r. Then

$$r = \sum_{\mu=1}^{n} (\gamma_\mu x_\mu), \tag{1}$$

where the γ_μ's are elements of an abstract algebra satisfying the relations $(\gamma_\mu\gamma_\nu + \gamma_\nu\gamma_\mu) = 2\delta_{\mu\nu}$.

The γ's can be expressed as matrices and for the case $n = 4$, they are the Dirac matrices.

(*b*) *The Dirac Equation.*—Let x_1, x_2, x_3 and x_4 $(= ict)$ be the co-ordinates of a world point, and similarly let p_1, p_2, p_3 and p_4 $(= iE/c)$ denote the components of the momentum four-vector. Besides x_4 and p_4, we shall also use the symbols x_0 and p_0 given by $x_4 = ix_0$ and $p_4 = ip_0$. Expressed as operators we have then $p_4 = -i\hbar\partial/\partial x_4$ and $p_0 = i\hbar\partial/\partial x_0$.

Now the momentum four-vector $\vec{P}$ is a vector with constant magnitude im_0c where m_0 is the rest mass of the particle. Apply now the result (1) to the vector $\vec{P} = (p_1, p_2, p_3, p_4)$. We then get

$$\sum_{i=1}^{4} \gamma_i p_i = im_0c. \tag{2}$$

If $|\psi\rangle$ is an eigenstate of the momentum four-vector, we get from (2) the equation of an electron as

$$\left(i\gamma_4 p_0 + \sum_{i=1}^{3} \gamma_i p_i - im_0c\right)|\psi\rangle = 0. \tag{3}$$

For the γ's we now choose the following representations:—

$$\gamma_4 = \begin{pmatrix} -\mathrm{I} & 0 \\ 0 & \mathrm{I} \end{pmatrix}; \quad \gamma_1 = \begin{pmatrix} 0 & -i\sigma_1 \\ i\sigma_1 & 0 \end{pmatrix}; \quad \gamma_2 = \begin{pmatrix} 0 & -i\sigma_2 \\ i\sigma_2 & 0 \end{pmatrix};$$

$$\gamma_3 = \begin{pmatrix} 0 & -i\sigma_3 \\ i\sigma_3 & 0 \end{pmatrix}$$

where I, σ_1, σ_2 and σ_3 denote respectively the unit matrix in two dimensions and the three Pauli matrices.

Multiplying (3) to the left by $-i\gamma_4^{-1}$, we get

$$\left(p_0 + \sum_{i=1}^{3} \alpha_i p_i + \beta m_0 c\right)|\psi\rangle = 0 \tag{4}$$

which is the Dirac equation in its conventional form.

When the electron is moving in a field, the components of the momentum four-vector are given by $(p_i + e/c\, \mathrm{A}_i)$ $(i = 0, 1, 2, 3)$ where A_0, A_1, A_2, A_3

are the scalar and vector potentials of the field. From the relations $\sum_{i=1}^{4} (p_i + e/c\, A_i)^2 = -\, m_0^2 c^2$, we see that the magnitude of the momentum four-vector is equal to im_0c in this case also. Thus by replacing p_i by $(p_i + e/c\, A_i)$ in (4), we get the equation for an electron moving in field as

$$\left\{\left(p_0 + \frac{e}{c} A_0\right) + \sum_{i=1}^{3} \alpha_i \left(p_i + \frac{e}{c} A_i\right) + \beta m_0 c\right\} | \psi \rangle = 0. \tag{5}$$

The left-hand side of (2) is similar in form to the expression of the length of a vector in terms of its direction cosines. The γ's can thus be regarded as the representations in a matrix algebra of the direction cosines of the momentum four-vector. We have thus

$$\gamma_i = \frac{p_i}{|\vec{P}|} \quad \text{or} \quad i\gamma_i = u_i, \tag{6}$$

where u_i $(i = 1, 2, 3, 4)$ are the components of the velocity four-vector. The matrices $i\gamma_i$ thus represent the components of the velocity four-vector.

Since

$$\alpha_i = -\, i\, (\gamma_4)^{-1}\, \gamma_i \quad (i = 1, 2, 3),$$

we have

$$\alpha_i = -\, \frac{ip_i}{p_4} = -\, \frac{\dot{x}_i}{c}$$

or

$$\dot{x}_i = -\, c\alpha_i. \tag{7}$$

Similarly

$$\beta = -\, \sqrt{1 - \frac{v^2}{c^2}}. \tag{8}$$

We thus get the well-known expressions for the components of the velocity of the particle without calculating the commutation relations of x_1, x_2 and x_3 with the Hamiltonian.

In finding out the dynamical variables that are the classical analogues of products (or quotients) of matrices, care should be taken to verify that only the algebraical rules that are common to both the matrix and the ordinary algebras are used. We have derived (4) by multiplying (2) by $-\, i\gamma_4^{-1}$ making use of the relation $(\gamma_4)^{-1}\, \gamma_4 = 1$ which is common to both algebras,

though one could equally well derive (4) by multiplying (2) by $-i\gamma_4$. The classical analogue of α_i is thus $-i(\gamma_4)^{-1}\gamma_i$ and not $-i\gamma_4\gamma_i$.

3. System of Many Electrons

We have seen that the Dirac equation can be derived by expressing the magnitude of the four-vector $\vec{P} + e/c\,\vec{A}$ in terms of its components. Now

$$\left(P_i + \frac{e}{c}A_i\right) = m_0 c u_i \qquad (i = 1, 2, 3, 4)$$

$$= \frac{m_0 \dot{x}_i}{\sqrt{1 - \frac{v^2}{c^2}}}, \tag{9}$$

where u_1, u_2, u_3, u_4 are the components of the velocity four-vector. natural way to generalise the Dirac equation for a system of particles would be to consider a four-vector whose components are respectively $\Sigma m_0 c u_i$ ($i = 1, 2, 3, 4$, or 0) where the sum is to be taken over all the particles of the system. We shall denote the components of this vector by $(P_0 + e/c\,A_0)$, $(P_1 + e/c\,A_1)$, $(P_2 + e/c\,A_2)$ and $(P_3 + e/c\,A_3)$.

Now in the special theory of relativity the components of the total momentum are given by[7]

$$P_i = -\frac{i}{c}\int T_{ik} dS_k + \Sigma m_0 c u_i, \tag{10}$$

where $T_{ik}..$ are the components of the energy-momentum tensor. In three-dimensional form, we can write for the total momentum of field *plus* charges

$$\int \frac{\mathbf{S}}{c^2}\, dV + \Sigma \boldsymbol{p} \tag{10 a}$$

and for the energy

$$\int W\, dV + \Sigma \mathcal{E}, \tag{10 b}$$

where

$$\mathbf{S} = \frac{c}{4\pi}\,\mathbf{E}\times\mathbf{H}$$

is the Poynting vector and

$$W = \frac{1}{8\pi}(E^2 + H^2)$$

is the density of the field energy. For a system of charges, the electrostatic energy (U), apart from the self-energy terms, is equal to

$$U = \int W dV = \sum \frac{e_A e_B}{r_{AB}}.$$

We thus see that the quantities

$$-\frac{e}{c}(A_0, A_1, A_2, A_3)$$

stand respectively for the energy-momentum of the field.

Let us denote the magnitude of $\vec{P} + e/c\,\vec{A}$ by iP'. P' is equal to $\sum_i m_{0i}c$ only as a first approximation. We have in fact

$$-P'^2 = -c^2\left(\sum_i m_i\right)^2 + \sum_{k=1}^{3}\left(\sum_{i=1}^{n} m_i \dot{x}_{ik}\right)^2, \tag{11}$$

where

$$m_i = \frac{m_{0i}}{\sqrt{1 - \frac{v_i^2}{c^2}}}.$$

Thus

$$-P'^2 = -c^2\left(\Sigma m_i^2 + 2\sum_{\substack{i,j \\ i<j}} m_i m_j\right) + \left(\sum_i m_i^2 v_i^2 + 2\sum_{\substack{i,j \\ i<j}} m_i m_j \mathbf{v}_i \cdot \mathbf{v}_j\right)$$

or

$$P'^2 = \Sigma m_i^2 c^2\left(1 - \frac{v_i^2}{c^2}\right) + 2\Sigma m_i m_j c^2\left(1 - \frac{\mathbf{v}_i \cdot \mathbf{v}_j}{c^2}\right). \tag{12}$$

Now

$$m_i m_j c^2\left(1 - \frac{\mathbf{v}_i \cdot \mathbf{v}_j}{c^2}\right) = \frac{m_{0i} m_{0j} c^2}{\sqrt{\left(1 - \frac{v_i^2}{c^2}\right)\left(1 - \frac{v_j^2}{c^2}\right)}}\left(1 - \frac{\mathbf{v}_i \cdot \mathbf{v}_j}{c^2}\right)$$

$$\sim m_{0i} m_{0j} c^2\left(1 + \frac{v_{ij}^2}{2c^2}\right), \tag{13}$$

where

$$v_{ij} = (v_i - v_j). \tag{14}$$

Substituting (13) in (12), we get

$$P'^2 \sim \Sigma m_{0i}{}^2c^2 + 2\Sigma m_{0i}m_{0j}c^2\left(1 + \frac{v_{ij}{}^2}{c^2}\right)$$

$$= (\Sigma m_{0i}c)^2 + \Sigma m_{0i}m_{0j}v_{ij}{}^2.$$

Thus a second approximation for P′ is given by

$$P' \sim \sum_{i=1}^{n} m_{0i}c + \tfrac{1}{2}\frac{\sum_{ij} m_{0i}m_{0j}v_{ij}{}^2}{\sum_{i} m_{0i}c}. \tag{15}$$

Applying now the results of Section 1 to the vector $\mathbf{P} + e/c\,\mathbf{A}$, we get the equation for the system of electrons as

$$\left\{\left(P_0 + \frac{e}{c}A_0\right) + \sum_{k=1}^{3} \alpha_k\left(P_k + \frac{e}{c}A_k\right) + \beta P'\right\}|\psi\rangle = 0. \tag{16}$$

4. Representation in the Product Space and The Breit Equation

Equation (16) describes the system as a whole and can be considered to be the equation of motion for the centre of inertia of the system. Since we are operating in a four-dimensional space, the matrices α_k and β are all four-dimensional. They refer to the entire-system of electrons and do not contain any labels of the individual particles. In practice, however, one needs equations that bring in explicitly the positions and spins of the individual electrons of the system. We shall see presently that Equation (16) can be transformed into one that contains explicit reference to the spins of the electrons if it is represented in the *product space* of the electrons.

Since the γ's represent the direction cosines of the momentum four-vector, their classical analogues are given by

$$\gamma_k = \frac{\sum_{i=1}^{n} m_i\dot{x}_{ik}}{iP'} \qquad (k = 1, 2, 3)$$

and

$$\gamma_4 = \frac{(\Sigma\, im_ic)}{iP'}. \tag{17 a}$$

Thus we have

$$\alpha_k = -\, i\,(\gamma_4)^{-1}\,\gamma_k = -\,\frac{\Sigma\, m_i \dot{x}_{ik}}{c\,\Sigma\, m_i}$$

and

$$\beta \mathrm{P}' = -\,\frac{\mathrm{P}'^2}{c\,\Sigma\, m_i}. \tag{17 b}$$

Thus we have

$$\sum_{k=1}^{3} \alpha_k \left(\mathrm{P}_k + \frac{e}{c}\mathrm{A}_k\right) + \beta \mathrm{P}'$$

$$= \frac{\left\{-\sum\limits_{k=1}^{3}\left(\sum\limits_i m_i \dot{x}_{ik}\right)^2 - \mathrm{P}'^2\right\}}{c\sum\limits_i m_i}$$

$$= -\sum m_i c = -\,c \sum_i \frac{m_{0i}}{\sqrt{\left(1 - \frac{v_i^2}{c^2}\right)}}$$

$$= -\sum_{i=1}^{n} m_{0i} c \sqrt{1 - \frac{v_i^2}{c^2}} - \frac{1}{c}\sum_{i=1}^{n} m_i v_i^2 \tag{18}$$

correct to terms of the order of v_i^4/c^3.

Alternatively, one can get (18) without using the idea of direction cosines at all. From (16) we have

$$\left\{\sum_{k=1}^{3} \alpha_k \left(\mathrm{P}_k + \frac{e}{c}\mathrm{A}_k\right) + \beta \mathrm{P}'\right\} |\, \psi \rangle = -\left(\mathrm{P}_0 + \frac{e}{c}\mathrm{A}_0\right) |\, \psi \rangle$$

and by definition,

$$-\left(\mathrm{P}_0 + \frac{e}{c}\mathrm{A}_0\right) = -\sum_i m_i c;$$

this leads now to the right-hand of (18).

For an electron moving in a field, we have

$$m\mathbf{v} = \mathbf{P} + \frac{e}{c}\mathbf{A}$$

where P is the momentum conjugate to the position of the particle and A is the vector potential of the field. Thus we have

$$\sum m_i v_i^2 = \sum \mathbf{v}_i \cdot \left(\mathbf{P}^i + \frac{e}{c}\mathbf{A}^i\right). \tag{19}$$

The term $e/c\,\Sigma\,\mathbf{v}_i \cdot \mathbf{A}^i$ gives the interaction energy of the charges with the magnetic field produced by the motion of the electrons.

Now the potentials arising from the motion of a charge e have been worked out in Landau and Lifshitz[7] and these are given by

$$\phi' = \frac{e}{r}\,; \quad \mathbf{A}' = e\,\frac{[\mathbf{v} + (\mathbf{v}\cdot\boldsymbol{n})\,\boldsymbol{n}]}{2cr}, \tag{20 a}$$

where r is the distance of the charge from the field point and $\boldsymbol{n} = \mathbf{r}/r$. When there are several charges we must sum over all the charges. Thus the potentials acting at the position of charge 1 due to the motions of charges 2, 3, $\cdots$, n are given by

$$\phi' = \sum_{j=2}^{n} \frac{e}{r_{1j}}$$

and

$$\mathbf{A}' = e \sum_{j=2}^{n} \frac{[\mathbf{v}_j + (\mathbf{v}_j \cdot \boldsymbol{n}_{1j})\,\boldsymbol{n}_{1j}]}{2cr_{1j}}. \tag{20 b}$$

Let us suppose that our system consists of n electrons moving in a static electric field $\mathrm{V}(\boldsymbol{r})$ (the field of the nuclei). We can write the potential energy of the system as

$$\mathrm{U} = -\,e\Phi = -\,e\sum_{i=1}^{n}\phi_i$$

where

$$\phi_i = \mathrm{V}(\boldsymbol{r}_i) - \frac{1}{2}\sum_{j}{}' \frac{e}{r_{ij}}.$$

The factor $\frac{1}{2}$ in the above expression for ϕ_i is introduced to take care that the interaction energy between two electrons is not counted twice. The energy is thus expressible as the sum of n different terms, each term standing for the energy density of a particle. Consider now ϕ_1. We have

$$\phi_1 = \mathrm{V}(r_1) - \frac{1}{2}\sum_j{}' \frac{e}{r_{1j}} ;$$

this can be interpreted as the potential at the field point of electron 1 due to the static field V (r) and the fields of ($n-1$) moving charges, each having a charge of $-e/2$. Thus the vector potential A^1 that arises as a consequence of the motion of electrons 2, 3, ..., n can be obtained by multiplying (20 *b*) by $-\frac{1}{2}$. We have

$$\phi_1 = \mathrm{V}(r_1) - \frac{1}{2}\sum_j{}' \frac{e}{r_{1j}} ;$$

$$\mathbf{A}^1 = -e\sum_j \frac{[\mathrm{v}_j + (\mathrm{v}_j \cdot n_{1j})\, n_{1j}]}{4cr_{1j}} . \tag{21}$$

In general we have

$$\mathbf{A}^i = -e\sum_j \frac{[\mathrm{v}_j + (\mathrm{v}_j \cdot n_{ij})\, n_{ij}]}{4cr_{ij}} .$$

Substituting (21) in (19) we get

$$\sum_{i=1}^{n} m_i v_i^2 = \sum_{i=1}^{n}{}' \mathrm{v}_i \cdot \mathrm{P}^i - \frac{e^2}{2c^2}\sum_{\substack{ij \\ i<j}} \frac{[\mathrm{v}_i \cdot \mathrm{v}_j + (\mathrm{v}_i \cdot n_{ij})(\mathrm{v}_j \cdot n_{ij})]}{r_{ij}} . \tag{22}$$

Substituting (22) in (18) we get

$$\sum_{k=1}^{3} a_k \left(\mathrm{P}_k + \frac{e}{c}\mathrm{A}_k\right) + \beta \mathrm{P}' = -\sum_i m_{0i}c\sqrt{1-\frac{v_i^2}{c^2}} - \frac{1}{c}\sum \mathrm{v}_i \cdot \mathrm{P}^i + \frac{e^2}{2c^3}\sum_{ij}\left[\frac{\mathrm{v}_i \cdot \mathrm{v}_j}{r_{ij}} + \frac{(\mathrm{v}_i \cdot r_{ij})(\mathrm{v}_i \cdot r_{ij})}{r_{ij}^3}\right. . \tag{23}$$

We have seen that the velocity of the electron is related to the spin matrices by means of the relations

$$\mathrm{v} = -ca$$

and

$$\beta = -\sqrt{1 - \frac{v^2}{c^2}}.$$

Let us therefore introduce a set of matrices α^i and β^i by means of the relations

$$v_i = -c\alpha^i$$

and

$$\beta^i = -\sqrt{1 - \frac{v_i^2}{c^2}}. \tag{24}$$

A representation for the matrices α^i and β in the product space of the electrons can be obtained by adopting the following rule[8]: If two physical systems a and b are compounded to form a total system c, then the system space H of c is R×G where R is the system space of a and G of b. In the system c obtained by composition, a Hermitean form $A \times I_2$ is associated with a quantity α of a and $I_1 \times B$ with β of b where A and B are the forms associated with α, β in R, G respectively, and I_1 and I_2 are the unit forms in R and G.

In the product space, therefore, the matrices α^i and β are given by

$$\alpha^i = I \times I \times I \ldots \times \alpha \times I \ldots \times I$$

and

$$\beta^i = I \times I \times I \ldots \times \beta \times I \ldots \times I. \tag{25}$$

In the above, the product contains n terms, and α and β occur in the i-th place; further the $\times$ denotes direct product multiplication. Substituting (25), (24) and (23) in (16), we get the equation for the system as

$$\left\{\left(P_0 + \frac{e}{c}A_0\right) + \sum_{i=1}^{n}\sum_{k=1}^{3} \alpha_k{}^i P_k{}^i + m_0 c\left(\sum_{i=1}^{n} \beta^i\right) + \frac{e^2}{2c}\left[\sum_{\substack{ij \\ i<j}} \frac{\alpha^i \cdot \alpha^j}{r_{ij}} + \sum_{\substack{ij \\ i<j}} \frac{(\alpha^i \cdot r_{ij})(\alpha^j \cdot r_{ij})}{r_{ij}^3}\right]\right\} \psi = 0. \tag{26}$$

For the case $n = 2$, the above equation reduces to the well-known Breit equation.

Summary

It is shown that the Dirac equation for an electron moving in a field can be derived by expressing the magnitude of the momentum four-vector in terms of its components. By considering a four-vector whose components denote the total momentum and energy of the particles, a relativistic equation for a system of several electrons has been derived. A representation of this equation has been made in the product space of the electrons and it is shown that for the special case of a system containing two electrons, it leads to the well-known Breit equation.

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